

PROVISIONAL SPECIFICATION

Specification No. 97001. Application No. 97001, dated 14th December 1964. Complete Specification left on 14th September 1965. (Application accepted 14th June 1966.)

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IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF O-NITROPHENOL TO O-AMINOPHENOL.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention.

THIS IS AN INVENTION BY HANDADY VENKATAKRISHNA UDUPA, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN AND PAYYALLUR NARAYANAN ANANTHA RAMAN, ALL OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA, ALL INDIAN CITIZENS.

This invention relates to improvements in or relating to the electrolytic reduction of o-nitrophenol to o-aminophenol.

Hitherto it has been the practice to reduce o-nitrophenol chemically by iron and hydrochloric acid.

This is open to objection in that the efficiency of reduction is low and the isolation of the product complicated.

The object of this invention is to obviate these disadvantages by reducing o-nitrophenol electrolytically using a rotating cathode.

To these ends, the invention broadly consists in reducing a suspension of o-nitrophenol in dilute sulphuric acid, preferably 10 per cent. strength or sodium sulphate bath, also preferably of the same strength, in a divided cell at a rotating copper cathode. The reduction is carried out at temperatures between 30° to 80°C. but preferably at 60°-65°C. using a current density range upto 40 amps/dm² but preferably 30 amp/dm². After electrolysis, the catholyte is steam distilled and any unreduced o-nitrophenol recovered and distilled under vacuum and cooled. The o-aminophenol sulphate separates out and this is filtered. The mother liquor is made up preferably to 10 per cent. free acid content and reused. The process is repeated 4 times at which stage the electrolyte is neutralised and o-aminophenol free base is liberated. The base is recrystallised from boiling water. o-Aminophenol sulphate is also recrystallised and free base liberated by addition of sodium carbonate or caustic soda. At each stage, the cathode is thoroughly washed with warm water containing dilute sulphuric acid.

When sodium sulphate bath is used, the free base is liberated from the catholyte by neutralising with acid and filtering. After filtering the free base, the mother liquor is reused again for further electrolysis.

The following typical examples are given to illustrate the invention :

EXAMPLE 1.

Catholyte :	2 litres of 10% sulphuric acid.
o-Nitrophenol taken :	500 g.
Current density :	30 amp/dm ²
Temperature :	60-65°C

Cathode :	Rotating disc type copper—Area 0.75 dm ²
Anolyte :	10% sulphuric acid.
Anode :	Lead
o-Aminophenol recovered :	432 g.
Current efficiency :	86.4%

The same electrolyte was used four times. The current efficiencies obtained were : 86.4 per cent., 86.9 per cent., 84.3 per cent. and 80.0 per cent.

EXAMPLE 2.

Catholyte :	400 ml of 10% sodium sulphate
o-Nitrophenol taken :	100 g.
Current density :	30 amp/dm ²
Temperature :	60-65°C.
Cathode :	Rotating disc type copper—Area 0.25 dm ²
Anolyte :	10% sulphuric acid
Anode :	Lead
o-Aminophenol recovered :	65.8 g.
Current efficiency :	84%

The following are among the main advantages of the invention :

(1) The electrolytic reduction of o-nitrophenol to o-aminophenol proceeds smoothly and high current efficiencies are obtained.

(2) The isolation of the product is simple and the reuse of the electrolyte has advantage in reducing the cost of the product.

(3) The use of rotating cathode has simplified the design of high amperage cells.

(4) The difficulty of o-aminophenol complexing with iron as in the case of chemical reduction is avoided and the product obtained by this technique is of high purity.

R. BHASKAR PAI

Patents Officer,

Council of Scientific & Industrial Research,

Dated this 11th day of December, 1964.

COMPLETE SPECIFICATION

Specification No. 97001, dated 14th December 1964.

IMPROVEMENTS IN OR RELATING TO THE ELECTROCHEMICAL REDUCTION OF O-NITROPHENOL TO O-AMINOPHENOL.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

THIS IS AN INVENTION BY HANDADY VENKATAKRISHNA UDUPA, SCIENTIST, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN, SCIENTIST, PAYYALLUR NARAYANAN ANANTHARAMAN, SENIOR SCIENTIFIC ASSISTANT, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA, ALL INDIAN CITIZENS.

This is an invention by Handady Venkatakrishna Udupa, Scientist, Gobichettipalayam Srinivasan Subramanian, Scientist, Payyallur Narayanan Anantharaman, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to improvements in or relating to the electrochemical reduction of o-nitrophenol to o-aminophenol using rotating cathode technique.

Hitherto it has been the practice to reduce o-nitrophenol chemically by iron and hydrochloric acid. Even when electrochemical reduction was employed, only stationary electrode conditions were used resulting in the use of low current density.

This is open to objection in that the efficiency of reduction is low and the isolation of the product complicated.

The object of this invention is to obviate these disadvantages by the modifications and improvements now effected by us.

To these ends, the invention broadly consists in reducing a suspension of o-nitrophenol in dilute sulphuric acid, preferably 10 per cent. strength or sodium sulphate bath also preferably of the same strength, containing additions of copper sulphate, preferably 0.1 per cent. in a divided cell at a rotating electrode, preferably of copper. The reduction is carried out at temperatures between 30° to 80°C. but preferably at 60°C. using a current density range upto 40 amp/dm² but preferably 30 amp/dm². After electrolysis the catholyte is steam-distilled and any unreduced o-nitrophenol is recovered and the electrolyte subjected to vacuum concentration. The o-aminophenol sulphate separates out and this is filtered. The filtrate is made up in strength to preferably 10 per cent. sulphuric acid (free acid) and reused. The process is repeated at least 4 times and at this stage the electrolyte is neutralised and o-aminophenol free base is liberated. The base is recrystallised from boiling water. o-Aminophenol sulphate is also recrystallised and free base is liberated by the addition of sodium carbonate or caustic soda. At this stage, the cathode is thoroughly washed with warm water containing dilute sulphuric acid.

When sodium sulphate bath is used, the free base is liberated from the catholyte by neutralising with anolyte acid and filtering. After filtering the free base the mother liquor is reused again for further electrolysis. The following typical examples are given to illustrate the invention.

EXAMPLE

Two litres of 10 per cent. sulphuric acid was taken as catholyte and 500 g. of o-nitrophenol and 20 g. of copper sulphate are added to it. 500 ml of 10 per cent. sulphuric acid was taken as anolyte in a porous pot. A disc type copper cathode of area 2.8 dm² was used as cathode and a strip of lead was used as anode. The cathode was rotated preferably at a peripheral velocity of 2 to 3 meters/sec. and a current of 50 amp was passed corresponding to a current density of 18 amp/dm². The experiment was conducted for a theoretical time of 11.5 hours and afterwards the solution was steam-distilled to free it from o-nitrophenol.

The resulting solution was concentrated under reduced pressure to 1/3 its volume and on cooling, the o-aminophenol sulphate separated which was filtered and the solution was made to 10 per cent. free acid and reused for the second time. The results are given below :

EXAMPLE 1.

Catholyte :	2 litres of 10% sulphuric acid 500 g. of o-nitrophenol
Cathode :	Disc-type copper (rotating)
Area :	2.8 dm ²
Current density :	18 amp/dm ²
o-Nitrophenol recovered :	80 g.
Current efficiency based on the nitrocompound reduced :	84%

EXAMPLE 2.

Catholyte :	2 litres of 10% sulphuric acid 500 g. of o-nitrophenol
Cathode :	Rotating disc-type copper
Area :	2.8 dm ²
Current density :	18 amp/dm ²
o-Nitrophenol recovered :	68 g.
Current efficiency based on the nitrocompound reduced :	86.4%

Material balance for o-nitrophenol in both the experiments are worked out and given below :

o-Nitrophenol.
equivalent.

EXAMPLE No. 1

o-Nitrophenol recovered :	80 g.	80 g.
o-Aminophenol obtained as solid :	140 g.	150 g.
o-Aminophenol in solution :	180 g.	240 g.
Total		470 g.
Unaccounted :	30 g.	6%

EXAMPLE No. 2

o-Nitrophenol recovered :	68 g.	68 g.
o-Aminophenol obtained as solid :	158 g.	200 g.
o-Aminophenol in solution :	160 g.	204 g.
Total		474 g.
Unaccounted :	28 g.	5.6%

The electrolyte after experiments was analysed for free sulphuric acid content and was found to contain 194.5 g. of sulphuric acid. The initial concentration of sulphuric acid was 364.5 g. so that a quantity of 100 ml of sulphuric acid was required to bring the strength of free acid to 10 per cent. This was done and the volume of the electrolyte was made upto 2

litres and the acid was reused in the same manner as shown in the above experiments four times, the current efficiency in each run almost remaining the same viz, 85 to 88 per cent.

We claim :

(1) A process for the electrochemical reduction of o-nitrophenol to o-aminophenol by taking the former in sulphuric acid or sodium sulphate solution, preferably 10 per cent strength and reducing at a stationary or rotating copper cathode at elevated temperatures upto 80°C using high current densities upto 40 amp/dm² and separating the o-aminophenol sulphate and reusing the electrolyte a number of times but not less than 3 times

(2) A process as in Claim (1) wherein when sulphuric acid bath is used, the o-aminophenol sulphate is recovered by concentrating the electrolyte under reduced pressure, after removing the o-nitrophenol by steam distillation and filtering and reusing the filtrate for further electrolysis.

(3) A process as in Claim (1) wherein when sodium sulphate bath is used, the o-aminophenol is recovered by neutralising the electrolyte with dilute acid preferably from anolyte and recovering the free base

(4) A process as claimed in any of the above claims in which the reduction is carried out using high current densities but preferably upto 20 amp/dm²

(5) A process as in any one of the above claims in which reduction is carried out at elevated temperatures but preferably upto 50-60°C

(6) A process as claimed above in which reduction is carried out in any of the catholyte but containing copper sulphate, preferably 0.1 per cent

(7) A process as claimed in any of the above claims in which the reduction is carried out in a cell containing a porous diaphragm in which sulphuric acid or sodium sulphate solution, preferably 10 per cent strength is taken and having an anode preferably of lead, lead silver or lead antimony alloy

(8) A process for the electro-chemical reduction of o-nitrophenol to o-aminophenol substantially as hereinbefore described

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Dated this 7th day of September 1965.